PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 10/00, 210/16, 4/26, 4/70, 4/80 | A2

(11) International Publication Number: WO 99/62967

(43) International Publication Date: 9 December 1999 (09.12.99)

(21) International Application Number: PCT/US99/11549

(22) International Filing Date: 26 May 1999 (26.05.99)

(30) Priority Data:
60/087,152 29 May 1998 (29.05.98) US

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: BENNETT, Alison, Margaret, Anne; 507 Falkirk Road, Wilmington, DE 19803 (US). FELDMAN, Jerald; 16 Cinnamon Drive, Hockessin, DE 19707 (US). MCCORD, Elizabeth, Forrester; 514 Hemlock Drive, Hockessin, DE 19707 (US).

(74) Agent: EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Steet, Wilmington, DE 19898 (US).

(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: COPOLYMERIZATION OF OLEFINS

(57) Abstract

Ethylene and/or propylene, and α–olefins may be copolymerized by contacting them with certain iron or cobalt complexes of selected 2,6–pyridinecarboxaldehydebis(imines) and 2,6–diacylpyridinebis(imines). The polymers produced, some of which are novel, are useful as molding resins.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

TITLE

COPOLYMERIZATION OF OLEFINS

FIELD OF THE INVENTION

Selected iron and cobalt complexes of 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacylpyridinebis(imines) are catalysts for the copolymerization of ethylene and/or propylene and α-olefins. Novel polymers may be produced.

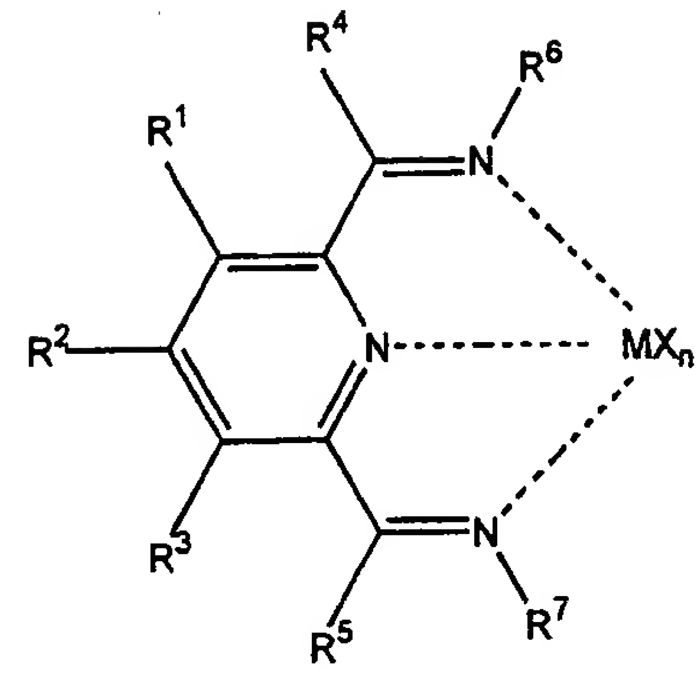
FIELD OF THE INVENTION

Copolymers of ethylene and/or propylene and α-olefins, such as linear low density polyethylene (LLDPE) are important items of commerce, millions of tons being produced annually. These polymers are used in a myriad of ways, such as for fiber, films, molding resins, etc. In most cases, ethylene and α-olefins are copolymerized using a catalyst, often a transition metal compound or complex. These catalysts may vary in cost per unit weight of polymer produced, the structure of the polymer produced, the possible need to remove the catalyst from the polymer, the toxicity of the catalyst, etc. Due to the commercial importance of copolymerizing ethylene, new polymerization catalysts are constantly being sought.

B. L. Small, et al., J. Am. Chem. Soc., vol. 120, p. 4049-4050 (1998), and G. J. P. Britovsek, et al., J. Chem. Soc., Chem. Commun., p. 849-850 (1998) report the polymerization of ethylene using catalysts containing Fe or Co complexes of 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacylpyridinebis(imines). Copolymerization of α-olefins and ethylene are not reported.

SUMMARY OF THE INVENTION

This invention concerns a first polymerization process, comprising, contacting, at a temperature of about -100°C to about +200°C, a compound of the formula



(II)

with one or both of ethylene and propylene, and an olefin of the formula $H_2C{=}CHR^{21}$ and:

(a) a first compound W, which is a neutral Lewis acid capable of abstracting X^- an alkyl group or a hydride group from M to form WX^-, $(WR^{20})^-$ or WH^- and which is also capable of transferring an alkyl group or a hydride to M, provided that WX^- is a weakly coordinating anion; or

(b) a combination of second compound which is capable of transferring an alkyl or hydride group to M and a third compound which is a neutral Lewis acid which is capable of abstracting X^-, a hydride or an alkyl group from M to form a weakly coordinating anion;

wherein:

M is Co or Fe;

each X is an anion;

n is 1, 2 or 3 so that the total number of negative charges on said anion or anions is equal to the oxidation state of a Fe or Co atom present in (II);

R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;

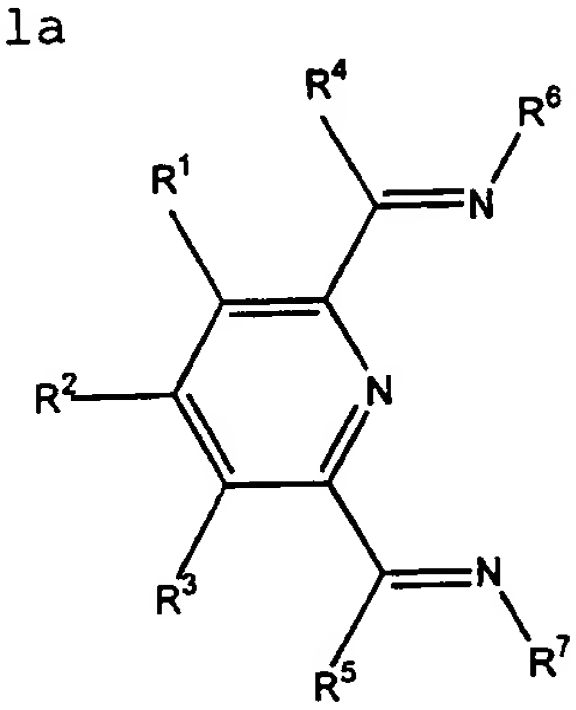
R^6 and R^7 are aryl or substituted aryl;

R^{20} is alkyl; and

R^{21} is alkyl.

This invention also concerns a second polymerization process, comprising contacting, at a

temperature of about -100°C to about +200°C, a Co[II], Co[III], Fe[II] or Fe[III] complex of a tridentate ligand of the formula



(I)

with one or both of ethylene and propylene, and an olefin of the formula $H_2C{=}CHR^{21}$ wherein:

R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

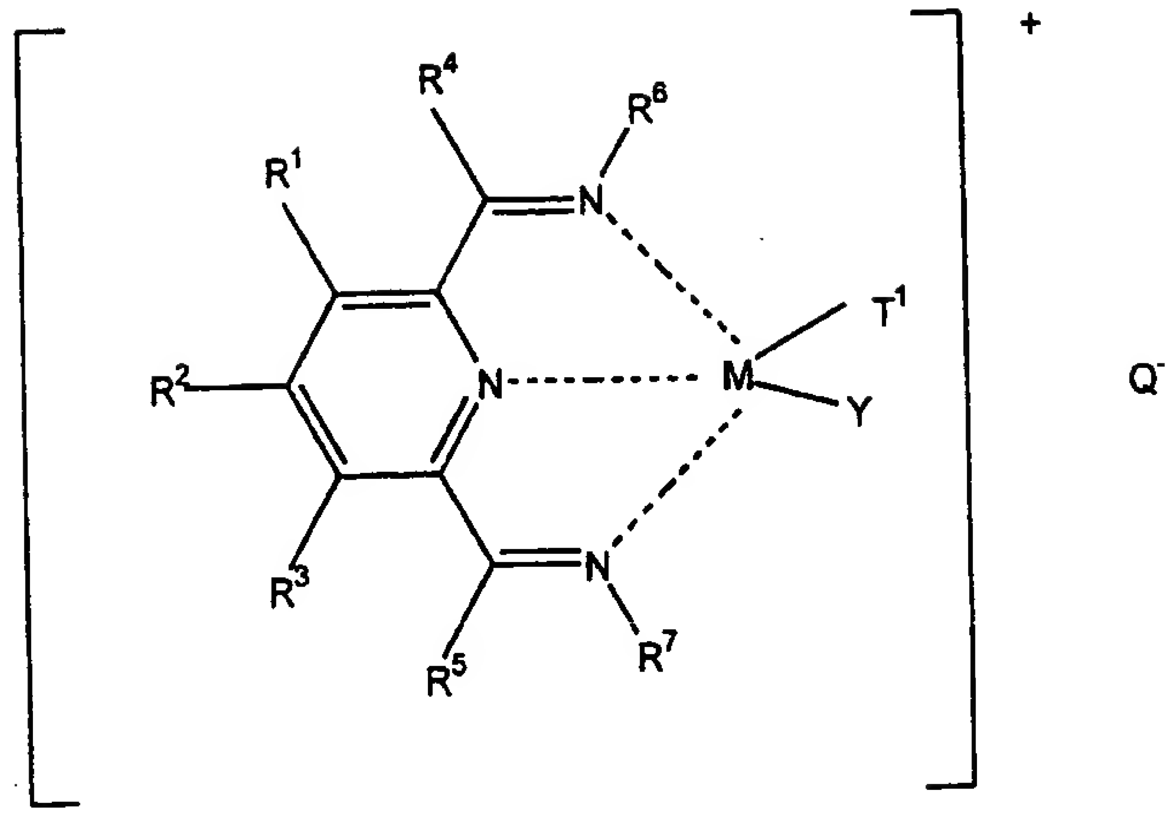
R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

R^{21} is alkyl;

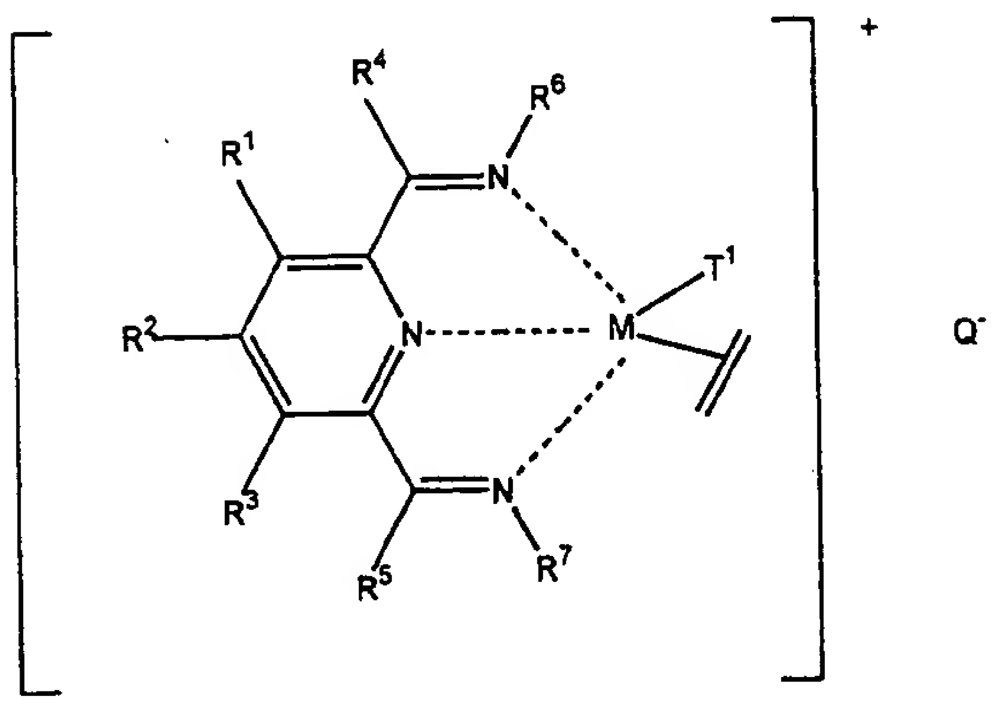
and provided that a Co[II], Co[III], Fe[II] or Fe[III] atom also has bonded to it an empty coordination site or a ligand that may be displaced by said ethylene, and a ligand that may add to said ethylene.

This invention also concerns a third polymerization process, comprising, contacting, at a temperature of about -100°C to about +200°C, one or both of ethylene and propylene, an olefin of the formula $H_2C{=}CHR^{21}$, and a compound of the formula



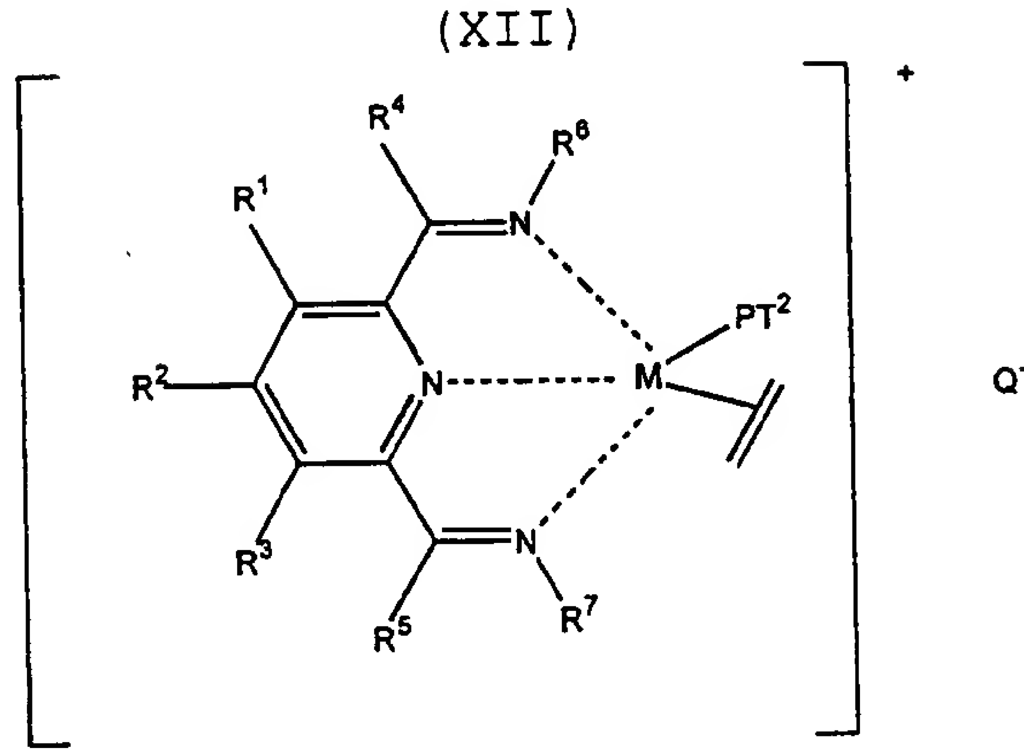
,

(VII)



, or

(XII)



(IX)

wherein:

M is Co or Fe;

R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

R^{21} is alkyl;

T^1 is hydride or alkyl or any other anionic ligand into which ethylene or an α-olefin can insert;

Y is a neutral ligand capable of being displaced by ethylene or a vacant coordination site;

Q is a relatively non-coordinating anion;

P is a divalent polyolefin group; and

T^2 is an end group.

DETAILS OF THE INVENTION

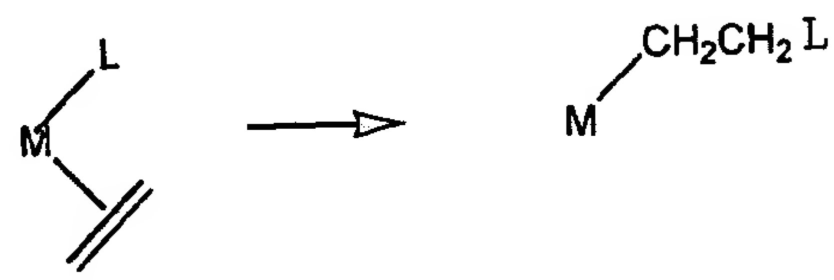
Herein, certain terms are used. Some of them are:

- A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.
- By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings. All of the hydrogen atoms may be substituted for, as in trifluoromethyl.
- By "(inert) functional group" herein is meant a group other than hydrocarbyl or substituted hydrocarbyl which is inert under the process conditions to which the compound containing the group is subjected. The functional groups also do not substantially interfere with any process described herein that the compound in which they are present may take part in. Examples of functional groups include halo (fluoro, chloro, bromo and iodo), ether such as $-OR^{18}$ wherein R^{18} is hydrocarbyl or substituted hydrocarbyl. In cases in which the functional group may be near a cobalt or iron atom, such as R^4 and R^5, the functional group should not coordinate to the metal

atom more strongly than the groups in compounds containing R^4 and R^5, which are shown as coordinating to the metal atom, that is they should not displace the desired coordinating group.

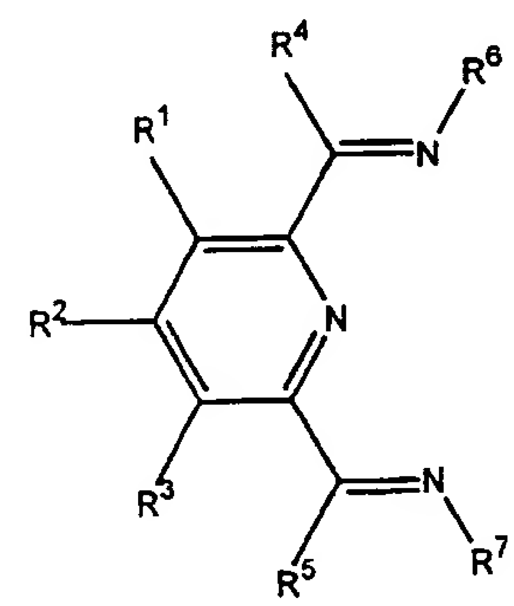
- By an "alkyl aluminum compound" is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as alkoxide, hydride, and halogen may also be bound to aluminum atoms in the compound.
- By "neutral Lewis base" is meant a compound, which is not an ion, which can act as a Lewis base. Examples of such compounds include ethers, amines, sulfides, and organic nitriles.
- By "cationic Lewis acid" is meant a cation which can act as a Lewis acid. Examples of such cations are sodium and silver cations.
- By relatively noncoordinating (or weakly coordinating) anions are meant those anions as are generally referred to in the art in this manner, and the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Stares, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by reference. Among such anions are those formed from the aluminum compounds in the immediately preceding paragraph and X^-, including $R^9{}_3AlX^-$, $R^9{}_2AlClX^-$, $R^9AlCl_2X^-$, and "R^9AlOX^-", wherein R^9 is alkyl. Other useful noncoordinating anions include BAF^- {BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, SbF_6^-, PF_6^-, and BF_4^-, trifluoromethanesulfonate, p-toluenesulfonate, $(R_fSO_2)_2N^-$, and $(C_6F_5)_4B^-$.
- By an empty coordination site is meant a potential coordination site that does not have a ligand bound to it. Thus if an ethylene molecule is in the proximity of the empty coordination site, the ethylene or other olefin molecule may coordinate to the metal atom.

- By a "divalent polyolefin group" is meant a group -Z- which contains one or more ethylene and/or α-olefin repeat units.
- By a ligand that may add to ethylene, propylene, or an α-olefin is meant a ligand coordinated to a metal atom into which an ethylene molecule (or a coordinated ethylene molecule) may insert to start or continue a polymerization. For instance, this may take the form of the reaction (wherein L is a ligand):



Note the similarity of the structure on the left-hand side of this equation to compound (IX) (see below).

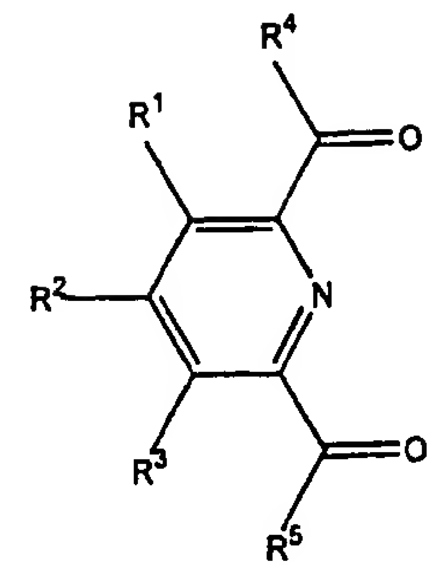
Compounds useful as ligands herein in iron and cobalt complexes are diimines of 2,6-pyridinedicarboxaldehyde or 2,6-diacylpyridines of the general formula



(IV)

wherein R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group, R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl, and R^6 and R^7 are aryl or substituted aryl.

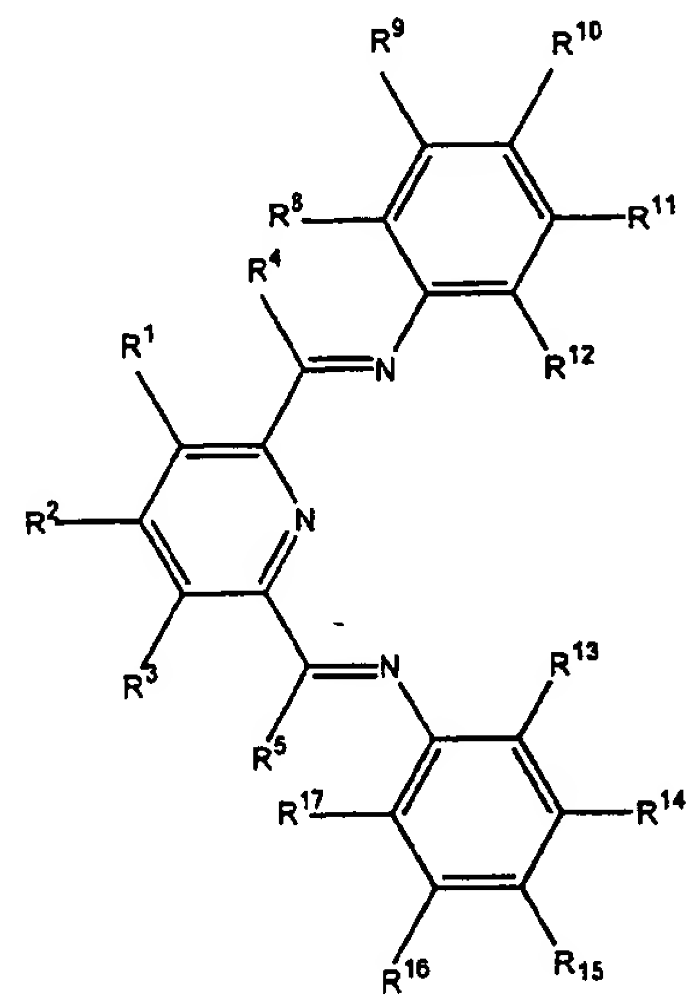
(IV) may be made by the reaction of a compound of the formula



(VI)

with a compound of the formula H_2NR^6 or H_2NR^7, wherein R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group, R^4 and R^5 are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, R^4 and R^5 are each hydrocarbyl or substituted hydrocarbyl, and R^6 and R^7 are aryl or substituted aryl. These reactions are often catalyzed by carboxylic acids, such as formic acid.

Preferred compounds of formula (IV) and compounds in which (IV) is a ligand are those of compound (III) [note



(III)

that (III) is a subset of (IV)], whether present in compounds such as (I), (II), (IV), (VII), (IX) and (XII). In (III), and hence in (I), (II), (IV) (VII), (IX) and (XII) that match the formula of (III), it is preferred that:

R^1, R^2 and R^3 are hydrogen; and/or

R^1 and R^3 are hydrogen and R^2 is trifluoromethyl; and/or

R^9, R^{10}, R^{11}, R^{14}, R^{15} and R^{16} is each independently halogen, alkyl containing 1 to 6 carbon atoms, or hydrogen, and it is more preferred that each of these is hydrogen; and/or

R^{10} and R^{15} are methyl; and/or

R^8 and R^{13} is each independently halogen, phenyl or alkyl containing 1 to 6 carbon atoms, and it is especially preferred that each R^8 and R^{13} is alkyl containing 1-6 carbon atoms and is more preferred that R^8 and R^{13} are methyl; and/or

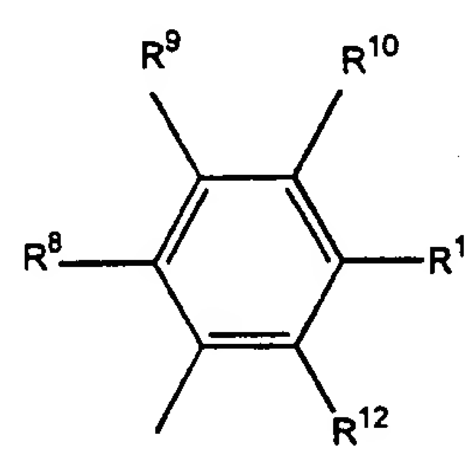
R^{12} and R^{17} is each independently halogen, phenyl, hydrogen, or alkyl containing 1 to 6 carbon atoms, and it is especially preferred that each R^{12} and R^{17} is alkyl containing 1-6 carbon atoms, and it is more preferred that R^{12} and R^{17} are methyl; and/or

R^4 and R^5 are each independently halogen, thioalkyl, hydrogen or alkyl containing 1 to 6 carbon atoms, and it is especially preferred that R^4 and R^5 are each independently hydrogen or methyl; and/or

R^8, R^{10}, R^{13}, R^{15} and R^{17} are hydrogen, and R^9, R^{11}, R^{14} and R^{16} are hydrocarbyl or substituted hydrocarbyl.

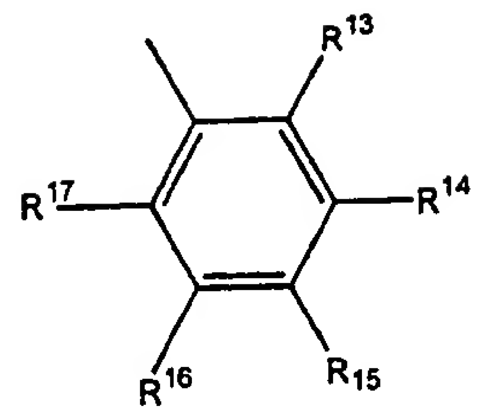
Also in (III), and hence in (I), (II), (IV) (VII), (IX) and (XII) that match the formula of (III), it is preferred that:

R^6 is



(X);

R^7 is



(XI);

R^8 and R^{13} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^9, R^{10}, R^{11}, R^{14}, R^{15} and R^{16} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} that are vicinal to one another, taken together may form a ring.

Specific preferred compounds (III) [and also in (I), (II), (IV), (VII), (IX) and (XII)] are:

R^1, R^2, R^3, R^9, R^{11}, R^{14} and R^{16} are hydrogen, and R^4, R^5, R^8, R^{10}, R^{12}, R^{13}, R^{15} and R^{17} are methyl;

R^1, R^2, R^3, R^9, R^{10}, R^{11}, R^{14}, R^{15} and R^{16} are hydrogen, R^8 and R^{13} are chloro, and R^4, R^5, R^{12} and R^{17} are methyl;

R^1, R^2, R^3, R^9, R^{10}, R^{11}, R^{12}, R^{14}, R^{15}, R^{16} and R^{17} are hydrogen, R^4 and R^5 are methyl, and R^8 and R^{13} are phenyl;

R^1, R^2, R^3, R^4, R^5, R^9, R^{10}, R^{11}, R^{14}, R^{15}, and R^{16} are hydrogen, and R^8, R^{12}, R^{13} and R^{17} are i-propyl; and

R^1, R^2, R^3, R^4, R^5, R^{10}, R^8, R^{10}, R^{13}, R^{15} and R^{17} are hydrogen, and R^9, R^{11}, R^{14} and R^{16} are trifluoromethyl.

In the polymerization processes described herein, it can be seen from the results that it is preferred that there be at least some steric crowding caused by the tridentate ligand about the Co or Fe atom. Therefore, it is preferred that groups close to the metal atom be relatively large. It is relatively

simple to control steric crowding if (III) is the tridentate ligand, since control of steric crowding can be achieved simply by controlling the size of R^8, R^{12}, R^{13} and R^{16}. These groups may also be part of fused ring systems, such as 9-anthracenyl.

In the first polymerization process it is preferred that X is chloride, bromide and tetrafluoroborate. It is also preferred that M is Fe[II] or Fe[III].

In the first polymerization process described herein an iron or cobalt complex (II) is contacted with ethylene, an α-olefin and a neutral Lewis acid W capable of abstracting X^-, hydride or alkyl from (II) to form a weakly coordinating anion, and must alkylate or be capable of adding a hydride ion to the metal atom, or an additional alkylating agent or an agent capable of adding a hydride anion to the metal atom must be present. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF_5, Ar_3B (wherein Ar is aryl), and BF_3. Suitable cationic Lewis acids or Bronsted acids include NaBAF, silver trifluoromethanesulfonate, HBF_4, or $[C_6H_5N(CH_3)_2]^+$ $[B(C_6F_5)_4]^-$. In those instances in which (II) (and similar catalysts which require the presence of a neutral Lewis acid or a cationic Lewis or Bronsted acid), does not contain an alkyl or hydride group already bonded to the metal atom, the neutral Lewis acid or a cationic Lewis or Bronsted acid also alkylates or adds a hydride to the metal or a separate alkylating or hydriding agent is present, i.e., causes an alkyl group or hydride to become bonded to the metal atom.

It is preferred that R^{20} contains 1 to 4 carbon atoms, and more preferred that R^{20} is methyl or ethyl.

For instance, alkyl aluminum compounds (see next paragraph) may alkylate (II). However, not all alkyl aluminum compounds may be strong enough Lewis acids to abstract X^- or an alkyl group from the metal atom. In

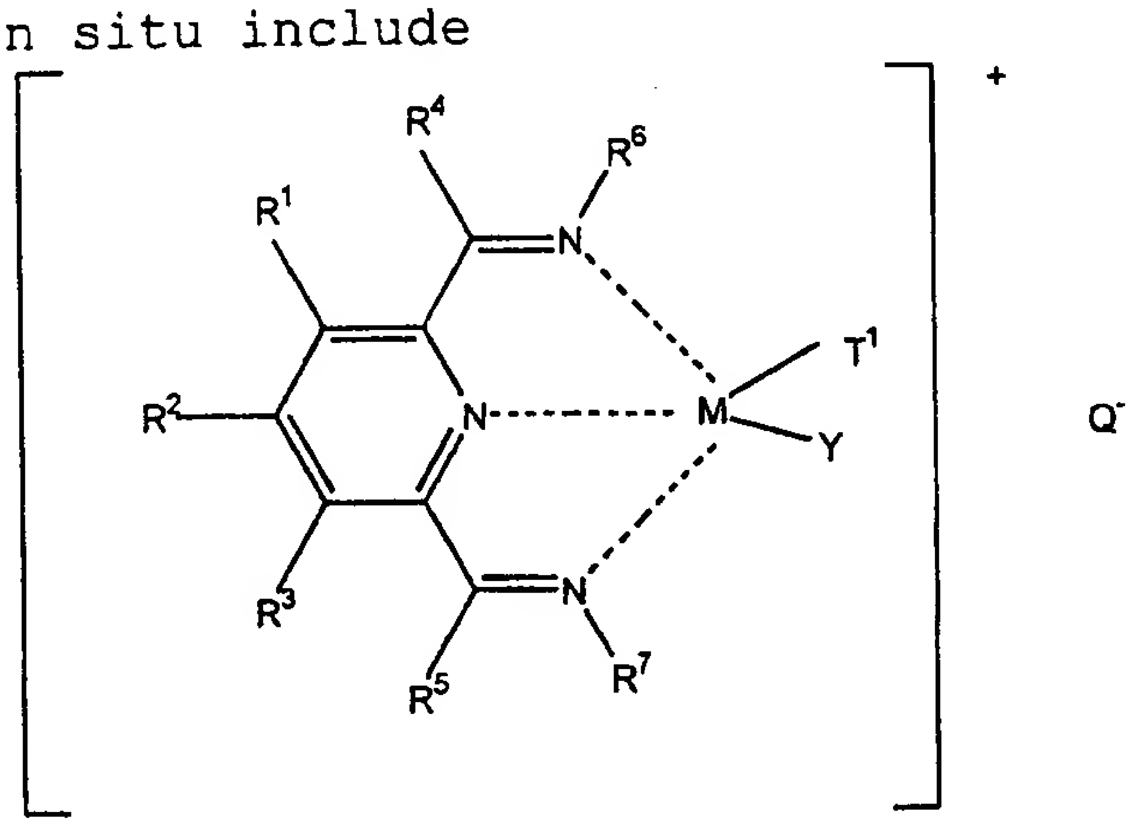
that case a separate Lewis acid strong enough to do the abstraction must be present.

A preferred neutral Lewis acid, which can alkylate the metal, is a selected alkyl aluminum compound, such as $R^{19}{}_3Al$, $R^{19}AlCl_2$, $R^{19}{}_2AlCl$, and "$R^{19}AlO$" (alkylaluminoxanes), wherein R^{19} is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Suitable alkyl aluminum compounds include methylaluminoxane (which is an oligomer with the general formula $[MeAlO]_n$), $(C_2H_5)_2AlCl$, $C_2H_5AlCl_2$, and $[(CH_3)_2CHCH_2]_3Al$.

Metal hydrides such as $NaBH_4$ may be used to bond hydride groups to the metal M.

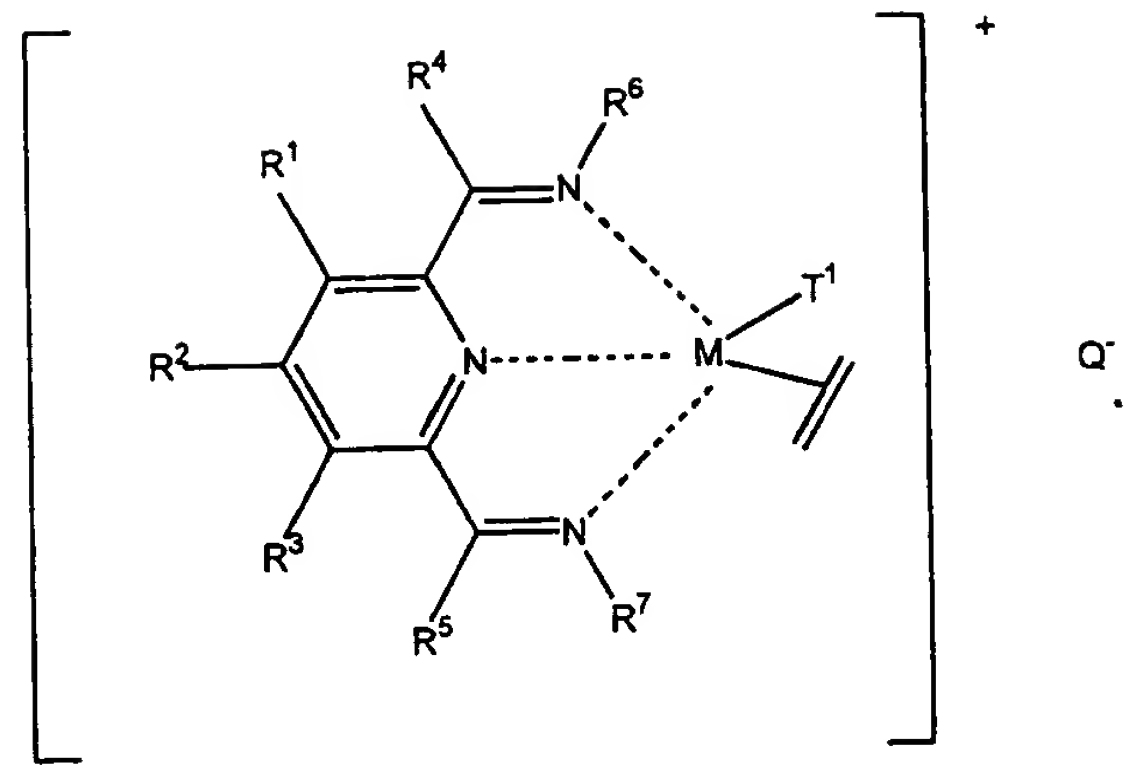
In the second polymerization process described herein a cobalt or iron complex of (I) is either added to the polymerization process or formed in situ in the process. In fact, more than one such complex may be formed during the course of the process, for instance formation of an initial complex and then reaction of that complex to form a living ended polymer containing such a complex.

Examples of such complexes which may be formed initially in situ include



(VII)

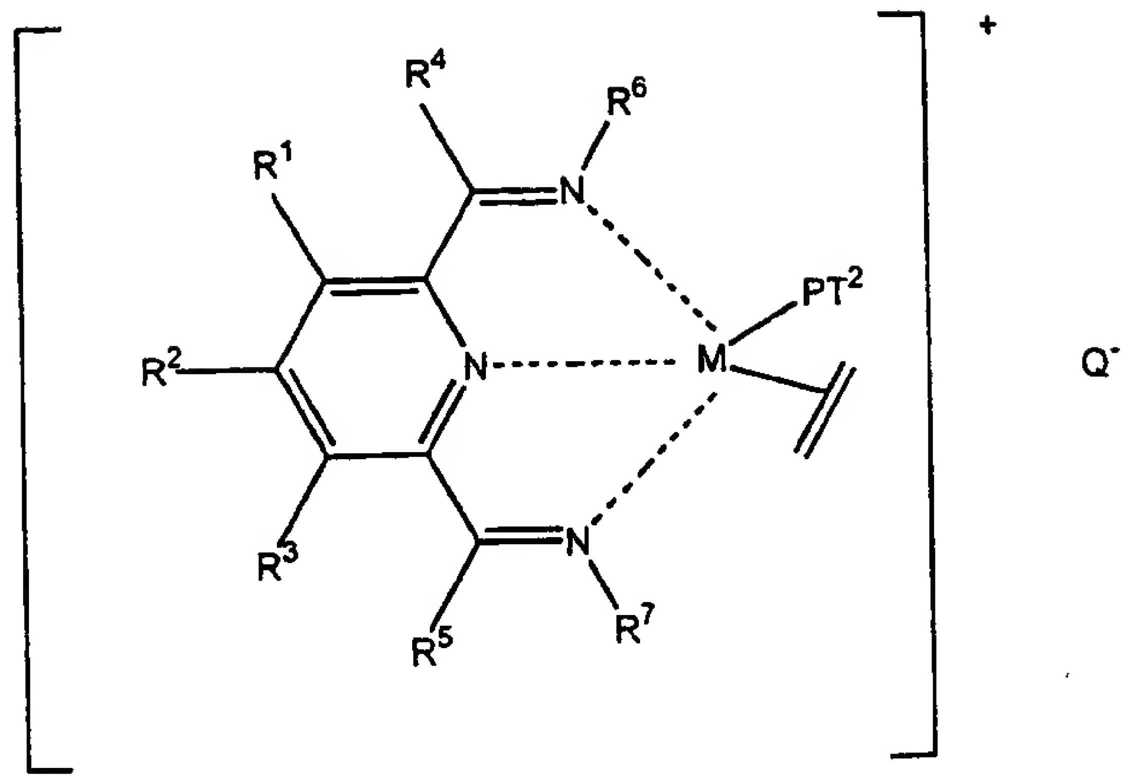
and



(XII)

wherein R^1 through R^7, and M are as defined above, T^1 is hydride or alkyl or any other anionic ligand into which ethylene or an α-olefin can insert, Y is a neutral ligand capable of being displaced by ethylene, propylene or an α-olefin, or a vacant coordination site, the "parallel lines" are an ethylene molecule coordinated to the metal, and Q is a relatively non-coordinating anion. Complexes may be added directly to the process or formed in situ. For instance, (VII) may be formed by the reaction of (II) with a neutral Lewis acid such as an alkyl aluminum compound. Another method of forming such a complex in situ is adding a suitable iron or cobalt compound such as iron [II] acetylacetonate, (I) and an alkyl aluminum compound. Other metal salts in which anions similar to acetylacetonate are present, and which may be removed by reaction with the Lewis or Bronsted acid. For instance metal halides and carboxylates (such as acetates) may be used, particularly if they are slightly soluble in the process medium. It is preferred that these precursor metal salts be at least somewhat soluble in the process medium.

After the polymerization has started, the complex may be in a form such as



(IX)

wherein R^1 through R^7, M, and Q are as defined above, and P is a divalent polymeric groups containing repeat units derived from ethylene and/or propylene and/or an α-olefin, and T^2 is an end group, for example the groups listed for T^1 above. Those skilled in the art will note that (IX) is in essence a polymer containing a so-called living end. It is preferred that M be in +2 oxidation state in (VII), (VIII) and (IX). Compounds such as (VII), (IX) and (XII) may or may not be stable away from an environment similar to that of the polymerization process, but they may be detected by NMR spectroscopy, particularly one or both of ^1H and ^{13}C NMR, and particularly at lower temperatures. Such techniques, especially for polymerization "intermediates" of these types are known, see for instance World Patent Application 96/23010, especially Examples 197-203, which is hereby included by reference.

(VII), (IX) and (XII) may also be used, in the absence of any "co-catalysts" or "activators" to polymerize ethylene in a third polymerization process. Except for the ingredients in the process, the process conditions for the third process, such as temperature, pressure, polymerization medium, etc., may be the same as for the first and second polymerization processes, and preferred conditions for those processes are also preferred for the third polymerization process.

In all the polymerization processes herein, the temperature at which the ethylene copolymerization is carried out is about -100°C to about +200°C, preferably about -60°C to about 150°C, more preferably about -50°C to about 100°C.

For copolymerization one or more α-olefins of the formula $H_2C{=}CHR^{21}$ may be used. It is preferred that R^{21} have 1 to 18 carbon atoms, more preferably 2 to 8 carbon atoms, and/or that R^{21} be n-alkyl. Since ethylene is polymerized considerably faster than propylene and most α-olefins by these catalysts, in order to obtain substantial incorporation of the α-olefin(s), the concentration of ethylene in the polymerization should preferably be relatively low compared to the concentration of the propylene and α-olefin(s). This will most often entail using ethylene at a low partial pressure, preferably less than 1.0 MPa, more preferably less than 500 kPa, and especially preferably less than 300 kPa (all these ethylene partial pressures are absolute partial pressures). If the α-olefin is a gas its partial pressure should preferably be relatively high. If the α-olefin is used in the liquid phase, its liquid concentration should preferably be relatively high.

NMR analysis of the product copolymers shows that the end groups are both saturated and unsaturated (olefinic), although saturated end groups usually outnumber unsaturated end groups. It is suspected that saturated end groups may arise through initiation and chain transfer involving alkyl aluminum compounds present in the polymerization. Unsaturated end groups are believed to arise though a β-hydride elimination-type mechanism. A small proportion of the olefinic ends appear to be internal olefins, but the majority of the olefinic ends are usually α-olefins (terminal olefins).

It is preferred that the product copolymer have at least 0.5 mole percent (total), more preferably 0.75

mole percent (total), especially preferably 1 mole percent (total), and highly preferably at least about 2 mole percent (total) of α-olefin(s) incorporated into the product copolymer. When 1-hexene is a comonomer the percent incorporated versus short chain branches, assuming all such branches are butyl, is shown in the following Table.

Mole Percent 1-Hexene	n-Butyl Branches per 1000 C Atoms
0.5	2.5
0.75	3.7
1.0	4.9
2.0	9.6
10.0	41.7

In copolymers of ethylene and $H_2C{=}CHR^{21}$ produced herein the polymer will contain $-R^{21}$ branches and methyl branches. The total amount of $H_2C{=}CHR^{21}$ is taken as the total of the $-R^{21}$ branches in the polymer, calculated according to a suitable formula, for example branches per 1000 carbon atoms or mole percent of $H_2C{=}CHR^{21}$ incorporated. It is believed that the methyl branches in the copolymer are associated with the end groups (but are not the end groups themselves). for example, end groups associated with methyl branches are

$$\sim\sim\sim\sim\sim CH_2CH(CH_3)CH_2CH_2CH_3 \text{ and}$$
$$\sim\sim\sim\sim\sim CH_2CH(CH_3)CH_2CH_2CH_2CH_3$$

are the methyl branch associated groups for 1-pentene and 1-hexene respectively (and similar structures for higher and lower homologs), wherein "~~~~" is the remainder of the polymer chain. Such groups are detectable by ^{13}C-NMR because methyl branches near the chain ends are somewhat different than methyl branches further in the interior of the polymer chain, see for instance the Examples herein. Note that the group beyond the methine carbon atom (towards the chain end) is actually $-R^{21}$. In other words the methyl branch is attached to the same carbon atom as an $-R^{21}$ group. Not

all polymer chains have such chain ends, but usually at least some of them are present in these copolymers.

A preferred monomer combination is ethylene and one or more olefins of the formula $H_2C=CHR^{21}$.

During the polymerization process often some or most of the olefin comonomer $H_2C=CHR^{21}$ will be unused in the polymerization. Testing of this unused comonomer at the end of the polymerization process shows that it is usually essentially unaltered (not isomerized), so it may be recovered and recycled into the polymerization, if desired. This recycling may take place without purification, or the comonomer may be purified being recycled to the polymerization, as by distillation.

The polymerization processes herein may be run in the presence of various liquids, particularly aprotic organic liquids. The catalyst system, ethylene, propylene, α-olefin, and polyolefin may be soluble or insoluble in these liquids, but obviously these liquids should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Specific useful solvents include hexane, toluene and benzene.

The copolymerizations herein may also initially be carried out in the solid state [assuming (II), (III) (IV) or (VII) is a solid] by, for instance, supporting (II), (III) (IV) or (VII) on a substrate such as silica or alumina or an organic substrate such as a polymer, activating it with the Lewis (such as W, for instance an alkylaluminum compound) or Bronsted acid and exposing it to an olefin. The support may also be able to take the place of the Lewis or Bronsted acid, for instance an acidic clay such as montmorillonite. Another method of making a supported catalyst is to start a polymerization or at least make an iron or cobalt complex of another olefin or oligomer of an olefin such as 1-hexene on a support such as silica or

alumina. These "heterogeneous" catalysts may be used to catalyze polymerization in the gas phase or the liquid phase. By gas phase is meant that the monomers are transported to contact with the catalyst particle while they are in the gas phase.

Hydrogen may be used as a chain transfer agent in all of the polymerization processes described herein.

In all of the polymerization processes described herein oligomers and copolymers of ethylene and/or propylene are made. They may range in molecular weight from oligomers, to lower molecular weight oils and waxes, to higher molecular weight polyolefins. One preferred product is a polymer with a degree of polymerization (DP) of about 10 or more, preferably about 40 or more. By "DP" is meant the average number of repeat (monomer) units in a polymer molecule.

In the Examples, the pressures given are gauge pressures. Methods of NMR analysis for polymer branching, and the notation used herein to describe the branching as determined by ^{13}C NMR, are found in U.S. Patent 5,880,241 (equivalent of World Patent Application 96/23010), which is hereby included by reference. Syntheses of the diimine ligands and their Co and Fe complexes are found in B. L. Small, et al., J. Am. Chem. Soc., vol. 120, p. 4049-4050 (1998), and G. J. P. Britovsek, et al., J. Chem. Soc., Chem. Commun., p. 849-850 (1998), which are both hereby included by reference. The following abbreviations and terms are used:

DSC - differential scanning calorimetry

GC - gas chromatography

GPC - gel permeation chromatography

HOF - heat of fusion

IBAO-0.65 - isobutylaluminoxane produced by the reaction of triisobutylaluminum with 0.65 equivalents of water

MMAO-3A - methylaluminoxane containing some isobutyl groups

Mn - number average molecular weight

MeOH - methanol

PMAO - polymethylaluminoxane

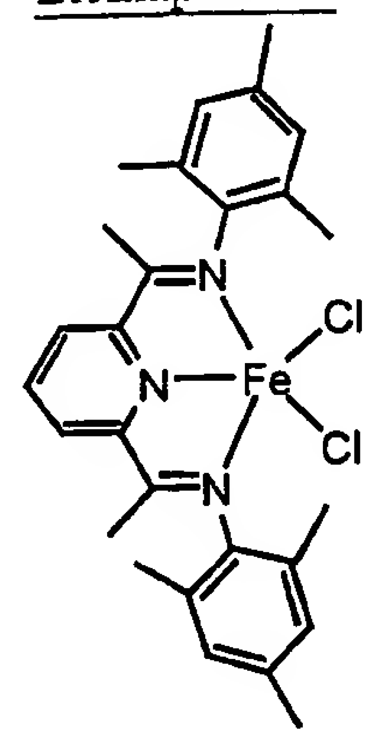
PMAO-IP - polymethylaluminoxane (Akzo, 12.8 weight percent aluminum in toluene)

PDI - weight average molecular weight divided by number average molecular weight (Mn)

TCB - 1,2,4-trichlorobenzene

Tm - melting point

Example 1



(XIII)

In a drybox under a nitrogen atmosphere, (XIII) (8 mg, 0.015 mmol) was weighed into a Schlenk flask and slurried in 20 ml anhydrous toluene. 1-Octene (3 ml, dried by distillation from sodium) was added and the Schlenk flask sealed and removed from the drybox. The flask was flushed well with ethylene and pressurized to 35 kPa. PMAO-IP (0.8 ml) was added and the solution turned orange and warmed. After 30 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 2.7 g white polymer. DSC (10°C/min, N_2); Tm = 123.2°C, shoulder on peak at 100°C. GPC (120°C, TCB); Mn = 1500, PDI = 5.6. The lowered (from pure polyethylene) melting point shows incorporation of comonomer.

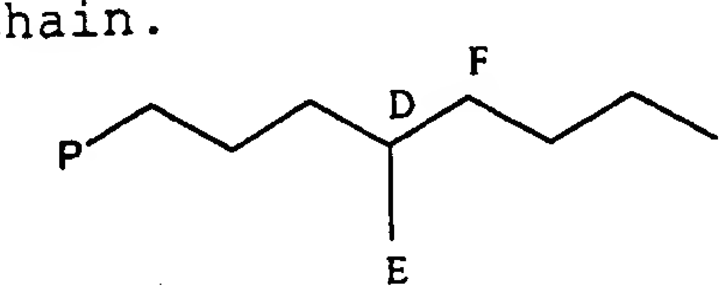
Example 2

In a drybox under a nitrogen atmosphere, (XIII) (7.5 mg, 0.014 mmol) was weighed into a Schlenk flask and slurried in 10 ml anhydrous toluene. 1-Hexene (3 ml, dried by distillation from sodium) was added and the Schlenk flask sealed and removed from the drybox. The flask was flushed well with ethylene and pressurized to 35 kPa. PMAO-IP (0.8 ml) was added and the solution turned green and warmed. After 30 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 6.0 g white polymer. DSC (10°C/min, N_2); Tm = 126.3°C, shoulder on low temperature side of peak. GPC (120°C, TCB); Mn = 2420, PDI = 8.0. ^{13}C-NMR analysis indicated a total of 2.5 mol% 1-hexene incorporation. The branching was >75% butyl branches (1,2 or 2,1 incorporation). Amyl and methyl branches were also observed at low levels. No ethyl or propyl branches were observed.

Example 3

In a drybox under a nitrogen atmosphere, (XIII) (2.0 mg) was weighed into a flask and slurried in 35 ml 1-hexene (Aldrich, 99+%, filtered through Al_2O_3 and stored over activated molecular sieves). The flask was stoppered and removed from the drybox. PMAO-IP (1.0 ml) was added to 5 ml anhydrous toluene and placed in a vial and removed from the drybox. The 1-hexene slurry was placed in a 100 ml Parr® stirred autoclave under an atmosphere of nitrogen. Stirring was started and the reactor heated to 50°C. The PMAO solution was then added to the reactor with 140 kPa ethylene. After 10 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 7.8 g white polymer. DSC (10°C /min., N_2); Tm = 102.0°C with a minor peak at 112.0°C. GPC (120°C, trichlorobenzene); Mn = 2534, PDI = 2.3. ^{13}C-NMR

analysis (5 weight percent in TCB, 120°C) indicated a total of 3.9 mol% 1-hexene incorporation. Of this most resulted in butyl branches (1,2 or 2,1 incorporation). Trace amounts of amyl and methyl branches were also observed. No ethyl or propyl branches were observed. The observed NMR is given below together with the assignments. The assignments of D, E and F are shown in the structure below, with "P" representing the rest of the polymer chain.



Frequency	PPM	Height	Assignment
3816.348	37.946	32.9	MB_4
3716.490	36.954	2.0	
3498.618	34.787	4.3	
3455.364	34.357	67.6	$\alpha\gamma^{+}B$
3415.848	33.964	36.4	$4B_4$
3320.796	33.019	2.7	D
3224.143	32.058	10.8	$3B_{6+}$, 3EOC
3052.729	30.354	75.6	$\gamma\gamma^{+}B$
3004.669	29.876	1417.0	$\gamma^{+}\gamma^{+}B$
2953.405	29.366	50.9	$3B_4$
2728.058	27.125	67.0	$\beta\gamma^{+}B$
2340.374	23.271	37.6	$2B_4$
2290.178	22.772	10.1	$2B_{5+}$, 2EOC
1994.877	19.835	2.3	E
1412.818	14.048	40.1	$1B_{4+}$, 1EOC

Example 4

In a drybox under a nitrogen atmosphere, (XIII) (6.1 mg, 0.011 mmol) was weighed into a Schlenk flask and slurried in 10 ml anhydrous toluene. 1-Hexene (5 ml, dried by distillation from sodium) and anhydrous toluene (15 ml) were added and the Schlenk flask sealed and removed from the drybox. The flask was cooled to 0°C and then flushed well with ethylene and pressurized to 35 kPa. PMAO-IP (0.9 ml) was added and the solution turned green and warmed. After 30 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and

finally acetone and dried under vacuum. Yield = 2.7 g white polymer. DSC (10°C/min, N_2); Tm = 127.6°C, shoulder on low temperature side of peak. GPC (120°C, trichlorobenzene); Mn = 2120, PDI = 19.1. ^{13}C-NMR analysis indicated a total of 1.2 mol% 1-hexene incorporation. Only methyl and butyl branches were observed (1,2 or 2,1 incorporation).

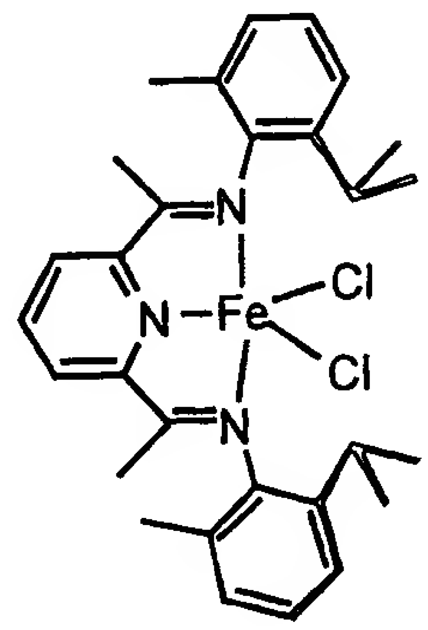
Comparative Example A

In a drybox under a nitrogen atmosphere, (XIII) (7.5 mg, 0.014 mmol) was weighed into a Schlenk flask and slurried in 10 ml anhydrous toluene. Anhydrous toluene (30 ml) was added and the Schlenk sealed and removed from the drybox. The flask was cooled to 0°C and then flushed well with ethylene and pressurized to 35 kPa. PMAO-IP (0.9 ml) was added and the solution turned orange and warmed. After 30 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.9 g white polymer. DSC (10°C/min, N_2); Tm = 132.7°C. GPC (120°C, trichlorobenzene); Mn = 2900, PDI = 19.1.

Example 5

In a drybox under nitrogen, (XIII) (1.8mg) was placed in 1-hexene (25 ml, Aldrich 99+%, filtered through activated Al_2O_3 and stored over activated molecular sieves) in a Hoke cylinder and sealed. PMAO-IP (0.9 ml) was placed in 2 ml anhydrous toluene in a vial and sealed. The containers were removed from the drybox. The 1-hexene slurry was placed in a Parr® stirred autoclave. Ethylene (70 kPa) was added, stirring started and the mixture heated to 75°C. The PMAO-IP solution was added to the reactor with an additional 160 kPa ethylene. After 81 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.61 g white polymer. DSC (10°C/min., N2); Tm(2nd heat) = 115.5°C. GPC (135°C, TCB); Mn = 1090, PDI = 1.8.

^{13}C-NMR analysis indicated a total of 1.4 mol% 1-hexene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 1.9, butyl 7.1 and amyl 1.4.



(XIV)

Example 6

In a drybox under nitrogen, (XIV) (6.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-hexene (10 ml, Aldrich 99+%, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 2.43g white polymer. DSC (10°C/min., N_2); Tm(2^{nd} heat) = 123.1°C, 109.2°C (broad). GPC (135°C, TCB); Mn = 1620, PDI = 8.4. ^{13}C-NMR analysis indicated a total of 2.1 mol% 1-hexene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 0.8, butyl 10.5 and amyl 1.5.

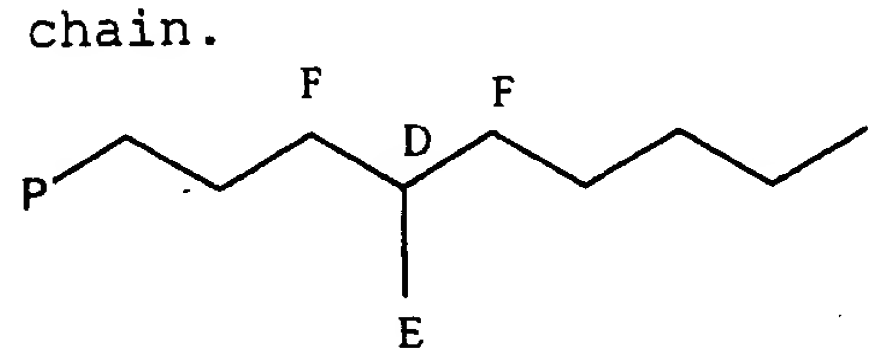
Example 7

In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-hexene (10 ml, Aldrich 99+%, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and MMAO-3A (0.45ml, Akzo, 6.42 wt% Al in heptane) added. After 30 min the reaction was quenched by addition of

MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.1 g white polymer. DSC (10°C/min., N_2); Tm(2nd heat) = 121.0°C, ~80°C (broad). GPC (135°C, TCB); Mn = 1507, PDI = 6.6. ^{13}C-NMR analysis indicated a total of 6.4 mol% 1-hexene incorporation. The observed number of short chain branches per 1000 CH_2 groups was methyl 1.9 butyl 30.5 and amyl 0.5. In addition, isobutyl ends are observed on the polymer (from the MMAO activator), and in this instance the isobutyl ends are not included in the methyl branch total.

Example 8

In a drybox under nitrogen, (XIII) (6.3 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-heptene (10 ml, distilled from Na) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.87g white polymer. DSC (10°C/min., N_2); Tm(2nd heat) = 122.3°C. GPC (135°C, TCB); Mn = 2680, PDI = 5.9. ^{13}C-NMR analysis (10 weight percent in TCB, 120°C) indicated a total of 5.3 mol% 1-heptene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 2.3, and amyl 24.6. The observed NMR is given below together with the assignments. The assignments of D, E and F are shown in the structure below, with "P" representing the rest of the polymer chain.



Frequency	PPM	Height	Assignment
3857.777	38.358	8.4	
3820.931	37.992	58.6	MB_{4+}
3750.443	37.291	7.4	F
3622.817	36.022	3.5	
3502.133	34.822	10.8	
3455.675	34.360	132.6	αB_{3+}
3398.004	33.787	4.6	
3323.778	33.049	4.9	D
3274.116	32.555	81.1	$3B_5$
3223.386	32.051	18.3	$3B_{6+}$, 3EOC
3142.218	31.243	7.9	
3080.808	30.633	30.3	
3051.438	30.341	108.0	$\gamma\gamma^{+}B$
3003.378	29.863	2327.2	$\gamma^{+}\gamma B$
2961.192	29.444	43.1	
2776.429	27.606	8.3	
2727.835	27.123	106.6	$\beta\gamma^{+}B$
2688.319	26.730	74.4	$4B_5$
2449.621	24.357	4.8	
2289.422	22.764	98.3	$2B_{5+}$, 2EOC
1994.654	19.833	4.8	E
1408.323	14.003	95.4	$1B_{4+}$, 1EOC

Comparative Example B

In a drybox under nitrogen, (XIII) (6.3 mg) was placed in a Schlenk flask and anhydrous toluene (15 ml added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.1 g white polymer. DSC (10°C/min., N_2); Tm(2^{nd} heat) = 127.2°C. GPC (135°C, TCB); Mn = 1220, PDI = 9.0. No branching was observed in the ^{13}C-NMR analysis.

Example 9

In a drybox under nitrogen, (XIV) (6.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-heptene (10 ml, distilled from Na) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was

filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.95 g white polymer. DSC (10°C/min., N_2); Tm(2[nd] heat) = 123.4°C, 110.6°C. GPC (135°C, trichlorobenzene); Mn = 2540, PDI = 5.3. ^{13}C-NMR analysis indicated a total of 3.0 mol% 1-heptene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 0.7, and amyl 14.4.

Comparative Example C

In a drybox under nitrogen, (XIV) (6.0 mg) was placed in a Schlenk flask and anhydrous toluene (15 ml) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. DSC (10°C/min., N_2); Tm(2[nd] heat) = 131.2°C. GPC (135°C, TCB); Mn = 1410, PDI = 20.0. No branching was observed in the ^{13}C-NMR analysis.

Example 10

In a drybox under nitrogen, (XIII) (6.1 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.82 g white polymer. DSC (10°C/min., N_2); Tm(2[nd] heat) = 117.8°C, ~90°C (broad). GPC (135°C, TCB); Mn = 1028, PDI = 3.8. ^{13}C-NMR analysis indicated a total of 10.0 mol% 1-pentene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 6.3, and propyl 50.9. GC analysis of the supernatant

indicated negligible isomerization of the unreacted 1-pentene.

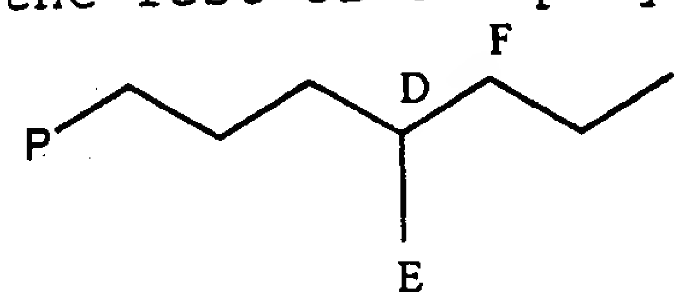
Example 11

In a drybox under nitrogen, (XIII) (1.4 mg) was placed in ~6 ml anhydrous toluene in a vial. 1-Pentene (30 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves), anhydrous toluene (5 ml) and PMAO (0.5ml, Akzo, 10.9 wt% Al in toluene) was placed in a Hoke cylinder and sealed. The containers were removed from the drybox. The 1-pentene slurry was placed in a 100ml Parr® stirred autoclave. Ethylene (41 kPa) was added and stirring started. The catalyst solution was added to the reactor with an additional 10psi ethylene. After 12 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.6 g white polymer. DSC (10°C/min., N_2); Tm(2nd heat) = 123.6°C. ^{13}C-NMR analysis indicated a total of 0.8 mol% 1-pentene incorporation.

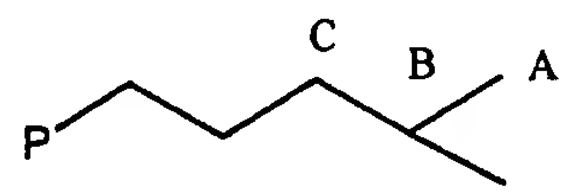
Example 12

In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and MMAO-3A (0.45 ml, Akzo, 6.42 wt% Al in heptane) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.9 g white polymer. DSC (10°C/min., N_2); Tm(2nd heat) = 128.0°C. GPC (135°C, TCB); Mn = 1716, PDI = 7.0. ^{13}C-NMR analysis (10 weight percent in TCB, 120°C) indicated a total of 4.5 mol% 1-pentene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 2.4, propyl 21.7, and amyl 0.4. Any isopropyl or isobutyl end

groups present due to initiator are not counted in the methyl group total. The observed NMR is given below together with the assignments. The assignments of A, B, C, D, E and F are shown in the structure below, with "P" representing the rest of the polymer chain.



and



Frequency	PPM	Height	Assignment
3990.433	39.677	6.8	F
3950.917	39.284	7.1	C
3829.166	38.074	5.9	
3792.320	37.708	53.3	MB_{3+}
3752.270	37.309	8.0	
3696.200	36.752	58.8	$3B_3$
3497.018	34.771	9.4	
3451.628	34.320	105.7	$\alpha\gamma^{+}B$
3398.228	33.789	5.0	
3293.031	32.743	7.2	$2B_5$, D
3222.543	32.042	21.0	$3B_{6+}$, 3EOC
3139.773	31.219	6.5	
3050.061	30.327	120.9	$\gamma\gamma^{+}B$
3002.535	29.855	2288.8	$\gamma^{+}\gamma^{+}B$
2960.883	29.440	56.7	
2823.646	28.076	8.6	B
2763.838	27.481	12.4	
2724.856	27.094	104.6	$\beta\gamma^{+}B$
2442.904	24.290	2.4	
2288.578	22.756	22.5	$2B_{5+}$,2EOC
2276.297	22.634	17.2	A
2029.055	20.175	63.0	$2B_3$
1987.937	19.766	8.0	E
1459.812	14.515	60.5	$1B_3$
1407.480	13.995	21.1	$1B_{4+}$, 1EOC

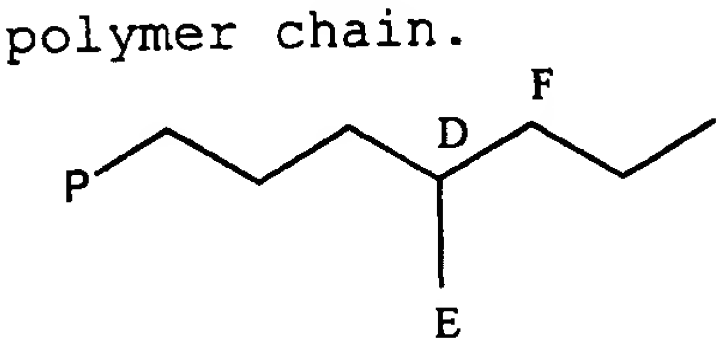
Example 13

In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The

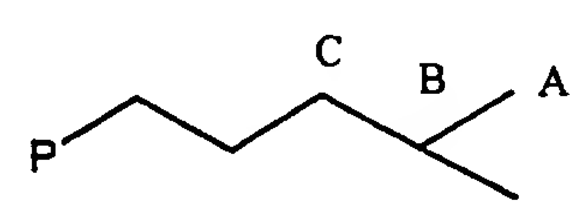
flask was sealed and removed from the drybox. The flask was flushed with ethylene and $AlEt_3$ (0.3 ml, 0.1M solution in toluene/hexane) and $B(C_6F_5)_3$ (0.0146 g in 0.5 ml toluene) were added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.21 g white polymer. DSC (10°C/min., N_2); Tm(2nd heat) = 127.6°C. ^{13}C-NMR analysis indicated a total of 0.64 mol% 1-pentene incorporation.

Example 14

In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and IBAO-0.65 (0.45ml, Akzo, 3.5 wt% Al in toluene) added. After 90 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. DSC (10°C/min., N_2); Tm(2nd heat) = 115.5°C (bimodal). GPC (135°C, TCB); Mn = 1957, PDI = 8.9. ^{13}C-NMR analysis (10 weight percent in TCB, 140°C) indicated a total of 8.2 mol% 1-pentene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 3.4, and propyl 39.0. (amyl not integrated due to overlap). Any isopropyl or isobutyl end groups present due to initiator are not counted in the methyl group total. The assignments of A, B, C, D, E and F are shown in the structure below, with "P" representing the rest of the polymer chain.



and



Frequency	PPM	Height	Assignment
3991.407	39.687	10.5	F
3951.357	39.289	8.9	C
3840.285	38.184	15.2	
3802.371	37.807	179.7	MB_{3+}
3753.243	37.319	16.2	
3706.251	36.852	200.4	$3B_3$
3577.023	35.567	5.4	
3509.740	34.898	27.2	
3462.214	34.425	345.1	$\alpha\gamma^{+}B$
3391.192	33.719	7.8	
3295.606	32.769	9.8	D
3271.576	32.530	8.2	$3B_5$
3218.710	32.004	21.9	$3B_{6+}$, 3EOC
3159.970	31.420	15.7	
3084.142	30.666	35.7	
3047.296	30.300	320.8	$\gamma\gamma^{+}B$
2998.168	29.811	3551.0	$\gamma^{+}\gamma^{+}B$
2954.915	29.381	64.8	
2822.483	28.064	10.4	B
2777.093	27.613	16.5	
2727.965	27.125	337.0	$\alpha\gamma^{+}B$
2565.629	25.510	3.9	
2455.091	24.411	13.7	
2282.076	22.691	24.5	$2B_{5+}$, 2EOC
2270.862	22.579	23.9	A
2029.494	20.180	216.3	$2B_3$
1986.774	19.755	13.3	E
1451.173	14.429	206.8	$1B_3$
1397.239	13.893	24.1	$1B_{4+}$, 1EOC
1355.054	13.473	6.7	

Note: Existence of Me branches implies that these do not arise from the activator.

Example 15

In a drybox under nitrogen, (XIII) (4.5 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 4-methyl-1-pentene (10 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 4.65 g white polymer. DSC (10°C/min., N_2); Tm(2^{nd}

heat) = 121.4°C, 100.6°C (broad). GPC (135°C, TCB); Mn = 1740, PDI = 5.0. ^{13}C-NMR analysis indicated a total of 4.1 mol% 4-methyl-1-pentene incorporation.

Example 16

In a dry box under nitrogen atmosphere, the iron complex 2,6-diacetylpyridinebis(2,4,6-trimethylphenylimine)iron dichloride (1.5 mg, 2.86 μmol) was weighed into a vial and diluted to 10 ml with toluene (Aldrich, Anhydrous 99.8%). An aliquot of 3 ml containing 0.45 mg (0.86 μmol) of catalyst was transferred to the injector vessel with 50 ml of toluene. To a second vessel, 100 ml of CaH_2 purified 1-octene (Aldrich, 98%) was mixed with 2 ml of MMAO-3A (Akzo Nobel). These solutions were transferred by pressure to a 600 ml Parr® autoclave reactor. The polymerization temperature was 120°C and the ethylene pressure was 860 kPa, adjusted by a pressure regulator. The polymerization was run for 30 min. The reaction was quenched with methanol. The solid polymer was filtered and washed with acetone. Yield = 2.68 g, DSC (10°C/min): Tm = 126.2°C, HOF = 212 J/g.

Example 17

In a dry box under nitrogen atmosphere, an aliquot of 3 ml from the same stock solution of Example 16 was diluted with 50 ml of toluene and transferred to the injector vessel. To the second vessel, 80 ml of CaH_2 purified 1-octene (Aldrich, 98%) was mixed with 2 ml of MMAO-3A (Akzo Nobel). These solutions were transferred by pressure to a 600 Parr® autoclave reactor. The polymerization temperature was 60°C and the ethylene pressure was 860 kPa, adjusted by a pressure regulator. The polymerization was run for 30 min. The reaction was quenched with methanol. The solid polymer was filtered, washed with acetone, and dried under vacuum. Yield = 38.9 g, DSC (10°C/min): Tm = 132.7 °C, HOF = 226 J/g.

Example 18

In a dry box under nitrogen atmosphere, the iron complex [2,6-diacetylpyridinebis{(3,5-trifluoromethyl)phenylimine}] iron dichloride was weighed (6 mg, 9.7 µmol) and diluted to 100 ml of toluene (Aldrich, anhydrous, 99.8%) and spiked with 20 drops of methylene chloride (Aldrich). To this solution, 5.6 ml of MMAO-3A (Akzo Nobel) was added. This catalyst solution was transferred via cannula to a feed vessel of a catalyst pump. The pumping rate was constant for 15 min, resulting in 3.8 mg of catalyst used. For the comonomer, 85 ml of CaH_2 purified 1-hexene (Aldrich, 99%) was transferred to the reactor through a feed vessel. A 500 ml Zipperclave® reactor was charged with 165 ml of hexane (Aldrich, anhydrous, 95%+). The polymerization was run at 50°C and 1.01 MPa of ethylene pressure. After 30 min, the reaction was quenched with methanol. The solid polymer was filtered, washed with acetone and dried under vacuum. Yield = 1.4 g, DSC (10°C/min): Tm = 126.6 °C, with a shoulder at about 118°C. HOF = 194 J/g. GPC Mw = 11345, PDI = 7.44.

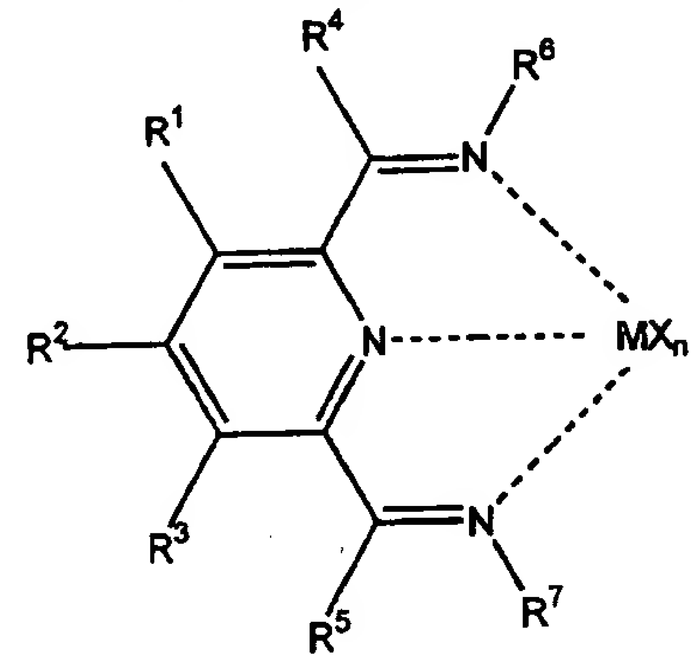
Comparative Example

Example 18 above was repeated with the same iron complex solution available in the catalyst pump feed vessel. No comonomer was added to this example. The catalyst pumping rate was constant for the first 15 min of the run, resulting in 2.3 mg of catalyst used. A 500 ml Zipperclave® reactor was charged with 250 ml of hexane (Aldrich, anhydrous, 95%). The polymerization was run at 50°C and 1.01 MPa of ethylene pressure. After 30 min, the reaction was quenched with methanol. The solid polymer was filtered, washed with acetone and dried under vacuum. Yield = 3.4 g, DSC (10°C/min): Tm = 130.3°C, HOF = 278 J/g. Mw = 14434, PDI = 6.03

CLAIMS

What is claimed is:

1. A polymerization process, comprising, contacting, at a temperature of about -100°C to about +200°C, a compound of the formula



(II)

with one or both of ethylene and propylene, an α-olefin of the formula $H_2C{=}CHR^{21}$, and:

(a) a first compound W, which is a neutral Lewis acid capable of abstracting X^- and alkyl group or a hydride group from M to form WX^-, WR^{20} or WH and which is also capable of transferring an alkyl group or a hydride to M, provided that WX^- is a weakly coordinating anion; or

(b) a combination of a second compound which is capable of transferring an alkyl or hydride group to M and a third compound which is a neutral Lewis acid which is capable of abstracting X^-, a hydride or an alkyl group from M to form a weakly coordinating anion;

wherein:

M is Co or Fe;

each X is an anion;

n is 1, 2 or 3 so that the total number of negative charges on said anion or anions is equal to the oxidation sate of a Fe or Co atom present in (II);

R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

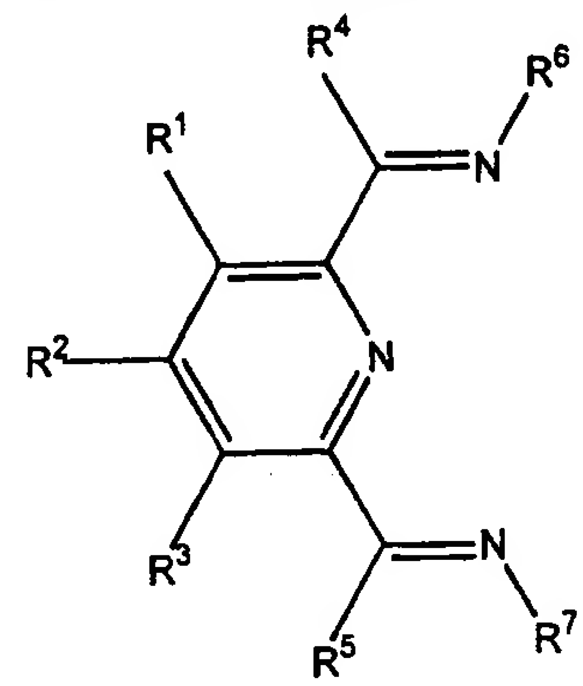
R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl;

R^6 and R^7 are aryl or substituted aryl;

R^{20} is alkyl; and

R^{21} is alkyl

2. A polymerization process, comprising contacting, at a temperature of about -100°C to about +200°C, a Co[II], Co[III], Fe[II] or Fe[III] complex of a tridentate ligand of the formula



(I)

with one or both of ethylene and propylene, and an α-olefin of the formula $H_2C{=}CHR^{21}$, wherein:

R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;

R^6 and R^7 are aryl or substituted aryl; and

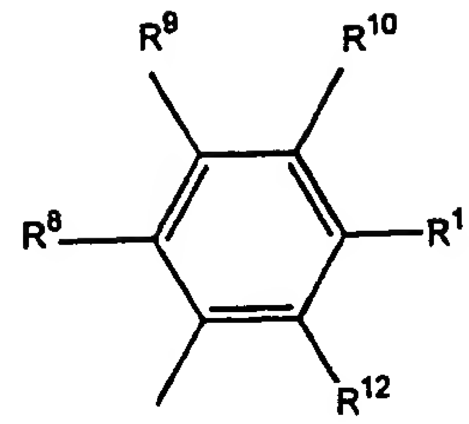
R^{21} is alkyl;

and provided that a Co[II], Co[III], Fe[II] or Fe[III] atom also has bonded to it an empty coordination site or a ligand that may be displaced by said ethylene, and a ligand that may add to said ethylene.

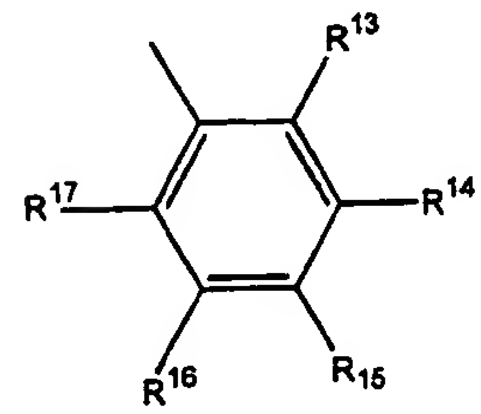
3. The process as recited in claim 1 or 2 wherein ethylene is present and propylene is not present.

4. The process as recited in claim 2 wherein:

R^6 is


(X);

R^7 is


(XI);

R^8 and R^{13} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^9, R^{10}, R^{11}, R^{14}, R^{15} and R^{16} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} that are vicinal to one another, taken together may form a ring.

5. The process as recited in claim 4 wherein:

R^1, R^2 and R^3 are hydrogen;

R^9, R^{10}, R^{11}, R^{14}, R^{15} and R^{16} is each independently halogen, alkyl containing 1 to 6 carbon atoms, or hydrogen;

R^8 and R^{13} is each independently halogen, phenyl or alkyl containing 1 to 6 carbon atoms;

R^{12} and R^{17} is each independently halogen, phenyl, hydrogen, or alkyl containing 1 to 6 carbon atoms; and

R^4 and R^5 are each independently hydrogen or alkyl containing 1 to 6 carbon atoms.

6. The process as recited in claim 5 wherein R^4 and R^5 are each hydrogen or methyl.

7. The process as recited in claim 5 wherein X is chloride, bromide or tetrafluoroborate.

8. The process as recited in claim 5 wherein said neutral Lewis acid is an alkyl aluminum compound.

9. The process as recited in claim 8 wherein said alkyl aluminum compound is polymethylaluminoxane.

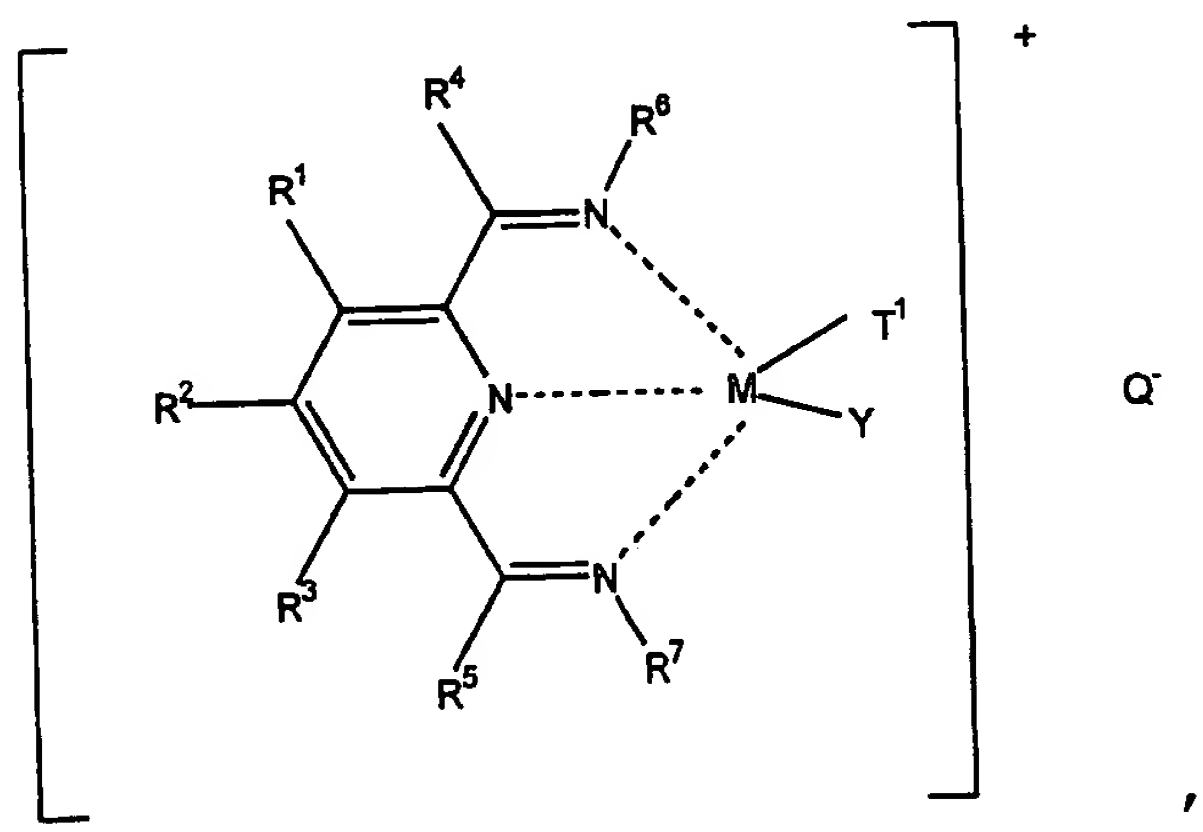
10. The process as recited in claim 5 wherein said temperature is about -50°C to about 100°C.

11. The process as recited in claim 1 wherein M is Fe.

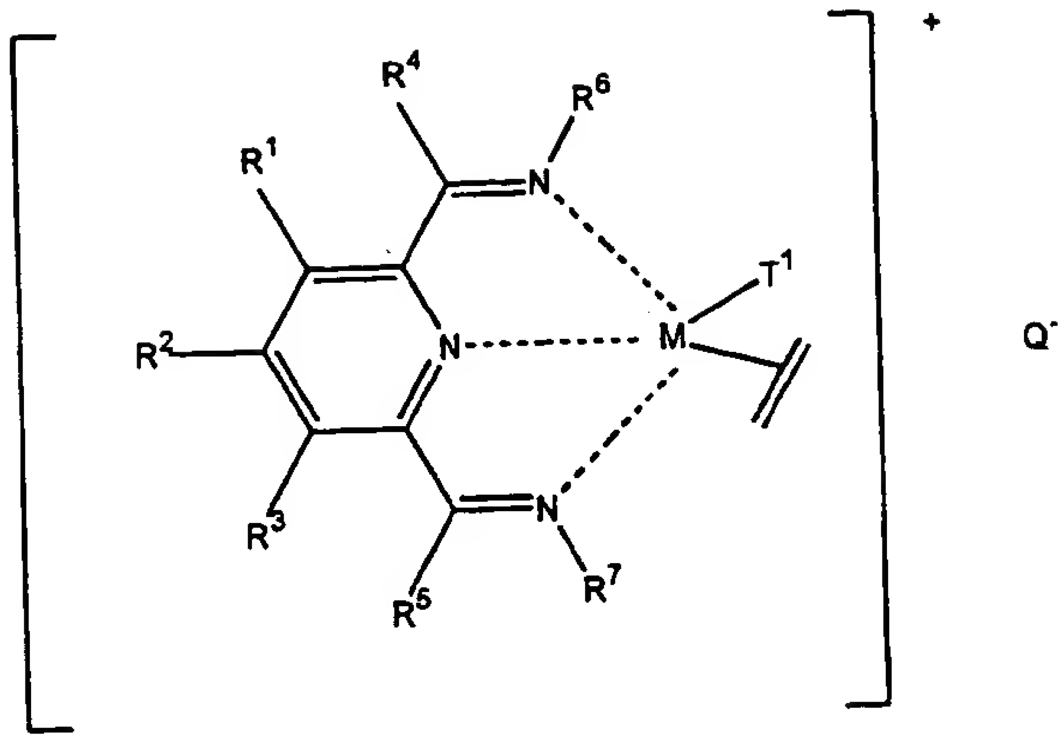
12. The process as recited in claim 2 wherein said complex is an Fe[II] or Fe[III] complex.

13. The process as recited in claim 1, 2, 11 or 12 wherein R^{21} is n-alkyl.

14. A polymerization process, comprising, contacting, at a temperature of about -100°C to about +200°C, one or both of ethylene and propylene, an α-olefin of the formula $H_2C{=}CHR^{21}$, and a compound of the formula

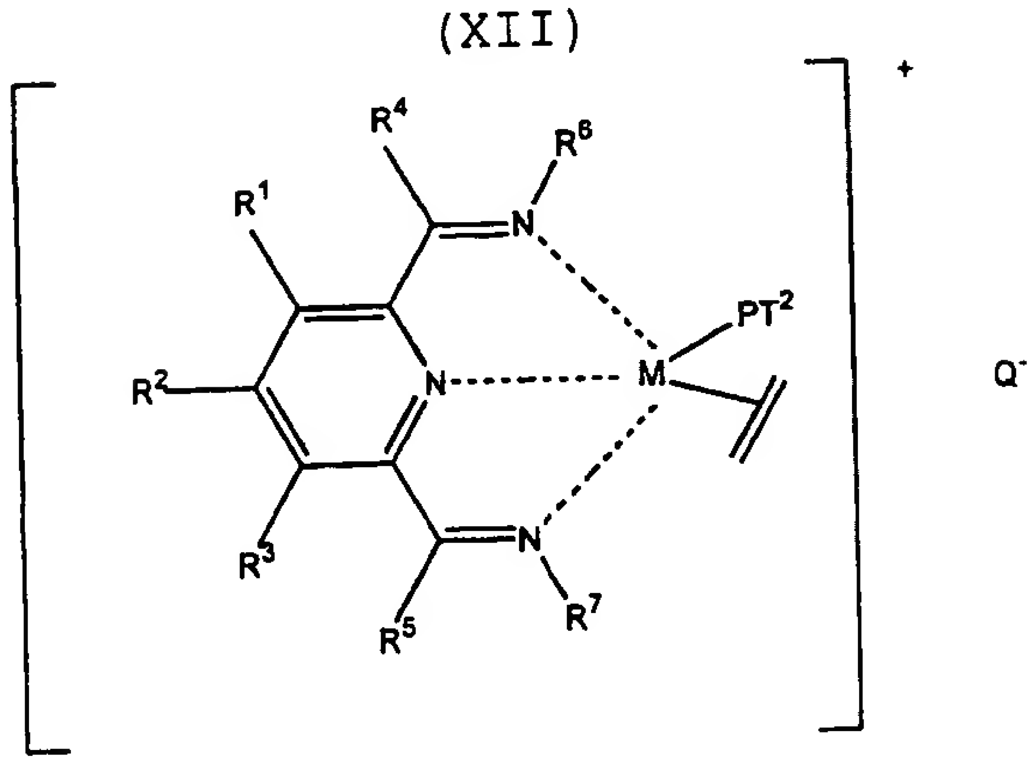


(VII)



, or

(XII)



(IX)

wherein:

M is Co or Fe;

R^1, R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;

R^6 and R^7 are aryl or substituted aryl;

R^{21} is alkyl;

T^1 is hydride or alkyl or any other anionic ligand into which ethylene or an α-olefin can insert;

Y is a neutral ligand capable of being displaced by ethylene or a vacant coordination site;

Q is a relatively non-coordinating anion;

P is a divalent polyolefin group; and

T^2 is an end group.

15. The process as recited in claim 14 wherein ethylene is present and propylene is not present.

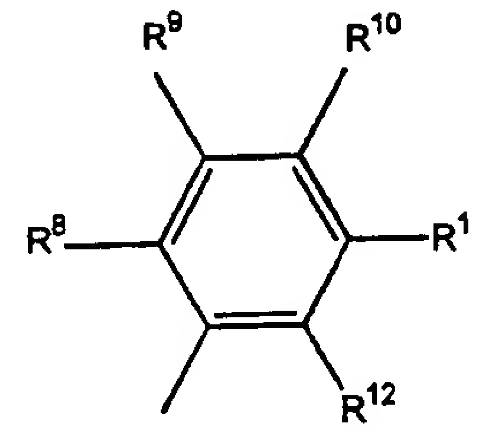
16. The process as recited in claim 15 wherein said compound is (VII).

17. The process as recited in claim 15 wherein said compound is (IX).

18. The process as recited in claim 15 wherein said compound is (XII).

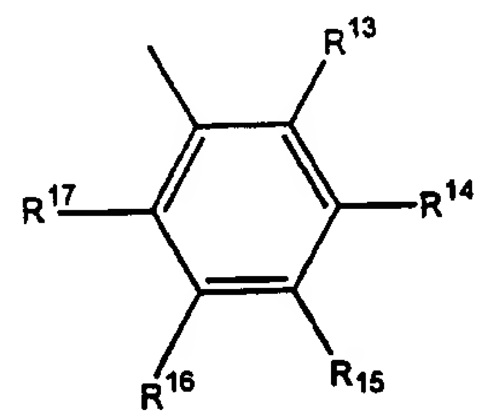
19. The process as recited in claim 15 wherein:

R^6 is



(X);

R^7 is



(XI);

R^8 and R^{13} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^9, R^{10}, R^{11}, R^{14}, R^{15} and R^{16} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} that are vicinal to one another, taken together may form a ring.

20. The process as recited in claim 15 wherein said temperature is about -50°C to about 100°C.

21. The process as recited in claim 15 wherein M is Fe.

22. The process as recited in claim 15 or 21 wherein R^{21} is n-alkyl.

23. A copolymer of ethylene and a one or more olefins of the formula $H_2C=CHR^{21}$ wherein said copolymer has methyl branches and $-R^{21}$ branches, and wherein the total of said branches indicate an incorporation of $H_2C=CHR^{21}$ of at least 0.5 mole percent.

24. The copolymer as recited in claim 23 wherein said incorporation is at least 1 mole percent.

25. The copolymer as recited in claim 23 or 24 wherein each of said methyl branches is attached to a carbon atom, and an $-R^{21}$ group is also attached to said carbon atom.

26. The copolymer as recited in claim 23 or 24 wherein R^{21} is n-alkyl.

27. The copolymer as recited in claim 25 wherein R^{21} is n-alkyl.

28. The process as recited in claim 1, 2 or 14 wherein said compound or complex is supported on a substrate.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 10/00, 210/16, 4/26, 4/70, 4/80 | A3

(11) International Publication Number: WO 99/62967

(43) International Publication Date: 9 December 1999 (09.12.99)

(21) International Application Number: PCT/US99/11549

(22) International Filing Date: 26 May 1999 (26.05.99)

(30) Priority Data:
60/087,152 29 May 1998 (29.05.98) US

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: BENNETT, Alison, Margaret, Anne; 507 Falkirk Road, Wilmington, DE 19803 (US). FELDMAN, Jerald; 16 Cinnamon Drive, Hockessin, DE 19707 (US). MCCORD, Elizabeth, Forrester; 514 Hemlock Drive, Hockessin, DE 19707 (US).

(74) Agent: EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Steet, Wilmington, DE 19898 (US).

(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(88) Date of publication of the international search report: 30 March 2000 (30.03.00)

(54) Title: COPOLYMERIZATION OF OLEFINS

(57) Abstract

Ethylene and/or propylene, and α–olefins may be copolymerized by contacting them with certain iron or cobalt complexes of selected 2,6–pyridinecarboxaldehydebis(imines) and 2,6–diacylpyridinebis(imines). The polymers produced, some of which are novel, are useful as molding resins.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/11549

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F210/16 C08F4/26 C08F4/70 C08F4/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	B.L. SMALL, M. BROOKHART AND A.M.A. BENNETT: "HIghly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene" J. AM. CHEM. SOC., vol. 120, no. 16, 29 April 1998 (1998-04-29), pages 4049-4050, XP002119954 cited in the application the whole document ---	1-22
A	EP 0 824 111 A (ATOCHEM ELF SA) 18 February 1998 (1998-02-18) page 9 ---	1-22
P,X	WO 98 27124 A (DU PONT) 25 June 1998 (1998-06-25) the whole document ---	1-22

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 October 1999	04.02.00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Golde, L

Form PCT/ISA/210 (second sheet) (July 1992)

International Application No
PCT/US 99/11549

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 98 30612 A (BROOKHART MAURICE S ;DU PONT (US); SMALL BROOKE L (US); UNIV NORTH) 16 July 1998 (1998-07-16) the whole document -----	1-22

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/11549

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 22

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-22

   A polymerization process comprising contacting at a temperature of -100 AC to 200 AC of (a) a very specific catalyst system with (b) one or both of ethylene and propylene and (c) an alpha-olefin of the formula H2C=CHR, where R is an alkyl group.

2. Claims: 23-28

   A copolymer of ethylene and one or more olefins of the formula H2C=CHR, where R is an alkyl group and wherein the copolymer has methylene branches and -R branches.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/11549

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0824111 A	18-02-1998	FR 2752238 A	13-02-1998
		CA 2209066 A	12-02-1998
		CN 1173504 A	18-02-1998
		JP 10081706 A	31-03-1998
WO 9827124 A	25-06-1998	AU 5711098 A	15-07-1998
		EP 0946609 A	06-10-1999
		NO 992930 A	10-08-1999
		US 5955555 A	21-09-1999
WO 9830612 A	16-07-1998	AU 6018198 A	03-08-1998
		EP 0951489 A	27-10-1999